

# Origin of ferromagnetism in $\text{Cs}_2\text{AgF}_4$ : importance of Ag - F covalency

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The magnetic nature of  $\text{Cs}_2\text{AgF}_4$ , an isoelectronic and isostructural analogue of  $\text{La}_2\text{CuO}_4$ , is analyzed using density functional calculations. The ground state is found to be ferromagnetic and nearly half metallic. We find strong hybridization of Ag- $d$  and F- $p$  states. Substantial moments reside on the F atoms, which is unusual for the halides and reflects the chemistry of the Ag(II) ions in this compound. This provides the mechanism for ferromagnetism, which we find to be itinerant in character, a result of a Stoner instability enhanced by Hund's coupling on the F.

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$\text{Cs}_2\text{AgF}_4$  is a member of a family of Ag(II) fluorides that form in perovskite and layered perovskite structures. The distinguishing feature is the presence of Ag(II), which is a powerful oxidizing agent.<sup>1,2</sup> This compound was first synthesized in 1974 by Odenthal and co-workers.<sup>3</sup> It occurs in the tetragonal  $\text{K}_2\text{NiF}_4$  layered perovskite structure. This is the same structure as the parent of the high temperature superconducting cuprates,  $\text{La}_2\text{CuO}_4$ .  $\text{Cs}_2\text{AgF}_4$  shows no tilts or rotations of the octahedra, which are common in oxide layered perovskites. Synthesis of isostructural  $\text{Na}_2\text{AgF}_4$  and  $\text{K}_2\text{AgF}_4$  was also reported and these compounds also have the  $\text{K}_2\text{NiF}_4$  structure. All three compounds are reported as being blue or purple in appearance and ferromagnetic. While transport measurements have not been reported for these compounds, it is known that the related distorted perovskite compound  $\text{KAgF}_3$  is metallic at high temperatures, and then has a metal insulator transition coincident with an antiferromagnetic ordering temperature.<sup>4</sup>

In the doped high- $T_c$  cuprates, superconductivity develops from a paramagnetic metallic phase, with Fermi surfaces coming from hybridized Cu  $d$  - O  $p$  bands. These are formally antibonding bands of  $d_{x^2-y^2}$  -  $p_\sigma$  character.<sup>5</sup> While the theory of high temperature cuprate superconductivity remains to be established, it is widely held that the phenomenon is associated with the physics of the undoped compounds, which are antiferromagnetic Mott insulators. Specifically, it is thought that there is a relationship between superconductivity and the antiferromagnetic fluctuations associated with the correlated  $d$  electrons of cuprates.  $\text{Cs}_2\text{AgF}_4$  has interesting similarities to the high- $T_c$  cuprates. As mentioned, it is isostructural, featuring  $\text{AgF}_2$  sheets in place of  $\text{CuO}_2$  sheets, it has a transition element with a  $d^9$  configuration, and it is magnetic. Moreover, related compounds have been shown both in band structure calculations and X-ray photoelectron spectroscopy experiments to display significant Ag - F covalency, reminiscent of the Cu - O hybridization in the cuprates.<sup>2,6,7</sup> These similarities and other considerations have led to speculations about possible high temperature superconductivity in Ag(II) fluorides.<sup>2,8</sup> One puzzling difference between the cuprates and the layered Ag(II) fluorides is that the undoped

cuprates are antiferromagnetic, while the argentates are ferromagnetic. One possible explanation would be an orbital ordering that favors ferromagnetism within a superexchange framework, as was recently suggested. However, neutron measurements did not detect the symmetry lowering that would occur in this case.<sup>9</sup>

Here we use electronic structure calculations to elucidate the electronic structure of  $\text{Cs}_2\text{AgF}_4$  and the origin of its magnetic properties. A previous density functional calculation for this material found it to be a covalent metal,<sup>2</sup> with a substantial density of states (DOS) at the Fermi level ( $E_F$ ) in the absence of magnetism.

We did electronic structure calculations within the local spin density approximation (LSDA) and the generalized gradient approximation (GGA),<sup>10,11</sup> using the general potential linearized augmented planewave method, with local orbitals,<sup>12,13</sup> as implemented in the WIEN2K program.<sup>14</sup> The augmented planewave plus local orbital extension was used for the Ag  $d$  and semicore levels.<sup>15</sup> The valence states were treated in a scalar relativistic approximation, while the core states were treated relativistically. Well converged basis set sizes and Brillouin zone samplings were employed. Except as noted otherwise, the LAPW sphere radii were 2.0  $a_0$  and 1.85  $a_0$  for the metal and fluorine atoms, respectively. The basis set cut-off was chosen to be  $RK_{max}=7.0$ , where  $R$  is the radius of the F sphere. We tested the convergence by comparison of LSDA results with an independent code, employing the LAPW augmentation with local orbitals and with higher basis set cut-offs as well as different sphere radii.

The structural data were obtained from the report<sup>3</sup> of Odenthal and co-workers:  $a = 4.58\text{\AA}$ ,  $c = 14.19\text{\AA}$ , including the two internal parameters corresponding to the Cs and apical F heights above the  $\text{AgF}_2$  square planar sheets. Minimization of the forces in the LDA approximation yielded a value of  $z_{\text{Cs}}=0.361$  and  $z_{\text{F}}=0.147$ , in close agreement with the experimental values of  $z_{\text{Cs}}=0.36$  and  $z_{\text{F}}=0.15$ .

Within the LSDA we find a  $\text{Cs}_2\text{AgF}_4$  to be a metal on the borderline of ferromagnetism. Fixed spin moment calculations showed a non-spin-polarized ground state, but with a 1  $\mu_B$  per formula unit fully polarized solution

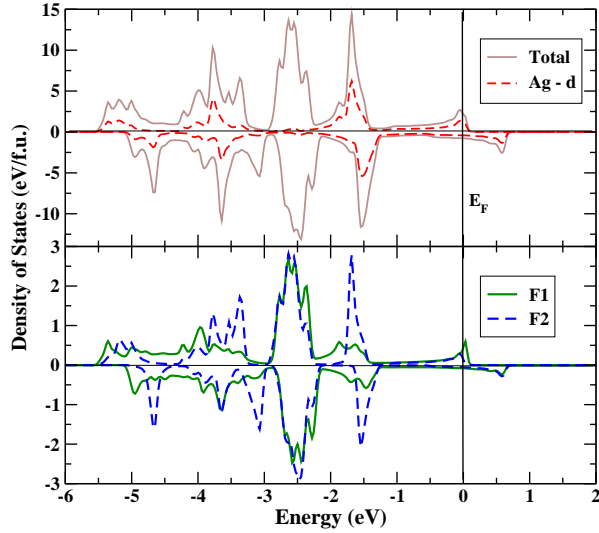


FIG. 1: (color online) Calculated DOS of ferromagnetic  $\text{Cs}_2\text{AgF}_4$ . *Top Panel*: The total (continuous/brown) and the orbitally resolved 4d states (dashed/red) of Ag, via projection onto the LAPW sphere. *Bottom Panel*: The orbitally resolved 2p states of the two types of Fluorine, F1 (continuous/green) and F2 (dashed/blue). Note the strong mixture of F and Ag states in the valence bands.

only 35 meV higher in energy. We also did LSDA calculations applying fields only inside the Ag LAPW spheres, which were chosen to be  $2.1 a_0$  in radius for this purpose. With 5 mRy fields of this type in a ferromagnetic pattern, moments of  $0.35 \mu_B$  were induced in the Ag spheres, and moments also appeared in the F spheres, for a total spin magnetization of  $0.62 \mu_B$ . Application of the same field in an in-plane  $c(2 \times 2)$  antiferromagnetic pattern yielded induced Ag moments in the spheres of only  $0.17 \mu_B$ , with a small moment also appearing on the apical F, but no moments on the in-plane F, as is required by symmetry. This shows the system to be much closer to ferromagnetism than antiferromagnetism at the LSDA level, and suggests an important role for the in-plane F in the magnetism.

Within the GGA, we obtain a ferromagnetic ground state, with spin magnetization,  $M = 0.9 \mu_B$  and energy 6 meV below the non-spin polarized solution. However, we do not find any metastable antiferromagnetic solution, implying itinerant magnetism, in particular, the absence of stable local moments. The calculated electronic density of states (DOS) for the ferromagnetic ground state is shown in Fig. 1. The band structure is shown in Fig. 2, and the Fermi surface in Fig. 3. The band structure is expected to be two dimensional, due to the bonding topology, which has  $180^\circ$  Ag-F-Ag links in the  $\text{AgF}_2$  sheets, but no direct Ag-F-Ag connections in the  $c$ -axis direction. This in fact is the case.<sup>16</sup> As may be seen,  $\text{Cs}_2\text{AgF}_4$  is close to a half metal, with the Fermi energy being near a band edge in the majority channel, but not in the minority channel. The minority spin Fermi surface consists of small hole cylinders running along the zone corner (from

the  $d_{x^2-y^2}$  band) and electron cylinders around the zone center  $\Gamma$  (from the  $d_{z^2}$  band). The majority spin Fermi surface consists of a single large square cylindrical electron surface that almost fills the Brillouin zone, leaving a small region of holes around the zone boundary.

$\text{Cs}_2\text{AgF}_4$  has two type of F sites forming distorted Ag centered octahedra; one is in the  $\text{AgF}_2$  sheets (referred as F1 in this paper), and the other is the apical F along the  $c$ -axis (referred as F2 in this paper). The apical Ag - F2 distance is slightly smaller than the in-plane Ag - F1 distance. A key point is that the F1 atoms bridge the Ag atoms in the sheets, with  $180^\circ$  bonds, while the apical, F2 atoms connect to only one Ag atom and therefore are not bridging.

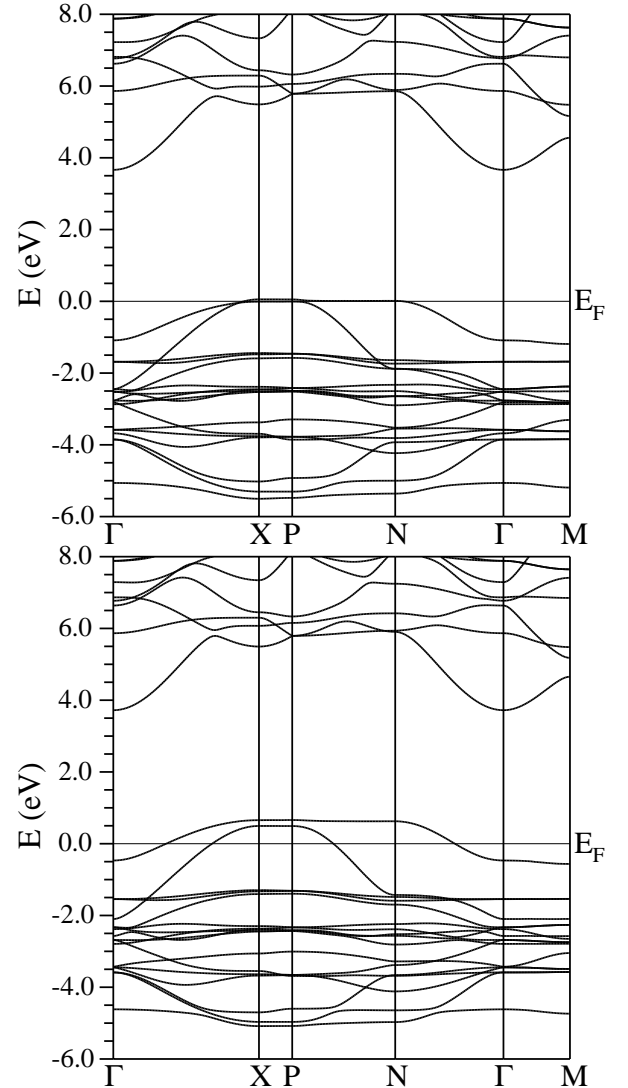


FIG. 2: GGA band structure of ferromagnetic  $\text{Cs}_2\text{AgF}_4$  using GGA, for majority (top) and minority (bottom) spins. Note the near half metallic character and the large gap between the hybridized Ag  $d$  - F  $p$  derived valence bands and the unoccupied Cs derived bands above.

Examining the DOS and projections in more detail, one may note that the valence bands have substantially mixed Ag  $d$  - F  $p$  character, especially near the bottom and top of the manifold where  $e_g$  -  $p_\sigma$  bonding and antibonding combinations occur. This hybridization involves both F1 and F2 atoms, and is consistent with previous results for Ag(II) fluorides.<sup>2,6,7</sup> The result is a very stable metallic electronic structure, with substantial F character at the Fermi energy,  $E_F$ , and a valence band width of  $\sim 5.5$  eV. This strong hybridization can be understood in chemical terms considering the very strongly oxidizing character of Ag(II), which in this compound partially oxidizes  $F^-$ . Thus covalency in this compound is a consequence of the unusual valence state of Ag. Turning to the band structure, there are two bands crossing  $E_F$  in the minority spin channel. These are the  $d_{x^2-y^2}$ , which hybridizes with the in-plane F, and the  $d_{z^2}$  hybridized with the apical F. The  $d_{x^2-y^2}$  - F1 combination has greater dispersion because of the in-plane topology, mentioned above. However, the  $d_{z^2}$  - F2 combination is higher lying, with the result that the two band maxima nearly coincide. The higher lying position of the  $d_{z^2}$  - F2 is readily explained by the fact that these bands are antibonding  $e_g$  -  $p_\sigma$  and the Ag - F2 bond is shorter. In the minority spin channel, the  $d_{z^2}$  band extends from -0.5 to 0.7 eV (relative to  $E_F$ ), while the  $d_{x^2-y^2}$  band extends from -2.1 to 0.5 eV. In the absence of the lighter  $d_{x^2-y^2}$

band, one would have a half-filled  $d_{z^2}$  band. Because the  $d_{x^2-y^2}$  is in fact present, the  $d_{z^2}$  is slightly electron doped away from half filling. This is in contrast to the cuprates, where only a  $d_{x^2-y^2}$  band is active, and this band is hole doped away from half-filling in the highest  $T_c$  compounds.

The small size of  $F^-$  relative to  $O^{2-}$  emphasizes the effect of the perovskite bonding topology in the band structure. This is because direct F - F hopping is reduced by its small size, relative to O in oxides, and the strongly oxidizing nature of F and Ag(II) push the Cs conduction bands to high energy, reducing the assisted hopping via Cs for the valence bands. Thus, the hopping is dominated by nearest neighbor Ag-F channels, so for example, the  $d_{xz} - p_\pi$  and  $d_{yz} - p_\pi$  derived bands take strong one dimensional character and are seen to be almost perfectly flat along some directions as seen in Fig. 2.

The mixed character of the bands is reflected in the distribution of the magnetic moments in the ferromagnetic ground state. Of the total spin moment of  $0.9 \mu_B$ , only  $0.5 \mu_B$  lies within the Ag LAPW sphere, radius  $2.0 a_0$ . The remaining  $\sim 40\%$  of the magnetization is F derived, approximately equally divided between the F1 and F2 sites. This is important for understanding the itinerant ferromagnetic ground state that we find. First of all, the large moments on the in-plane F1 atoms seen both in the GGA ferromagnetic ground state and in the LSDA calculations with ferromagnetic fields in the Ag (but not the F) spheres, mean that there is a contribution to the energy from the F polarization.  $F^-$  is a relatively small anion, at the end of the first row of the periodic table. Thus, when magnetic, it can have a strong Hund's coupling. This provides a generalized double exchange mechanism for favoring ferromagnetism, similar to the mechanism in  $SrRuO_3$ .<sup>17,18</sup> In the ferromagnetic case, the F1 atoms take moments due to the hybridized character of the bands around  $E_F$  and contribute to the Stoner instability through their Hund's coupling. With antiferromagnetic ordering, no induced moments can be present on the F1 atoms by symmetry, and therefore the Hund's coupling on these sites cannot stabilize the magnetism. Thus, the fact that the moments become unstable in an in-plane antiferromagnetic configuration supports this picture. Different from the ruthenates, the hybridized states in  $Cs_2AgF_4$  involve  $e_g$  instead of  $t_{2g}$  states, and the  $F^-$  ion is much smaller than  $O^{2-}$ .

We studied the stability of this ferromagnetic, two-band electronic structure, using LDA+U calculations and treating the Coulomb  $U$  as a parameter. We found, as expected, that a local moment, insulating state could be obtained. However this only happened when using a very high value  $U=7$  eV. This is an unreasonably large value for a  $4d$  ion in a screening environment. The reason for the weak effect of more realistic values of  $U$  is that the bands are strongly hybridized, and are really mixed F  $p$  - Ag  $d$  bands, and not narrow bands built from the Ag  $d$  orbitals. Thus we conclude that on-site Coulomb correlations do not have a large effect on the electronic

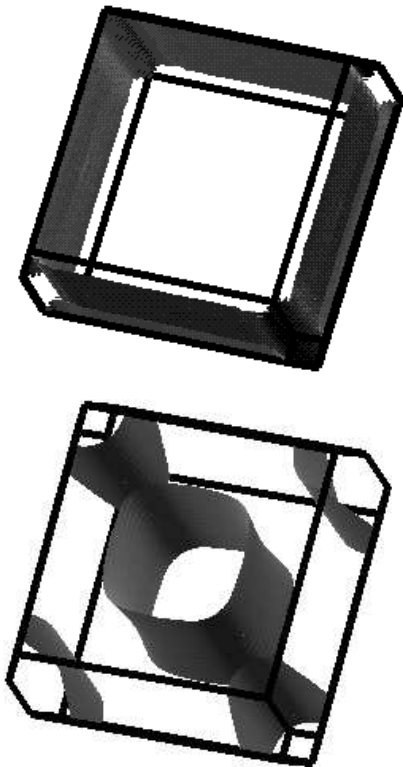


FIG. 3: GGA majority (top) and minority (bottom) Fermi surfaces of ferromagnetic  $Cs_2AgF_4$ .

structure or magnetism of this compound. This is in contrast to the undoped cuprates, where the LSDA and GGA approximations incorrectly predict non-magnetic metallic ground states, and the Hubbard  $U$  is crucial for obtaining moment formation and an insulating ground state.

To summarize, density functional calculations of the electronic structure of  $\text{Cs}_2\text{AgF}_4$  show strong covalency between Ag  $d$  and F  $p$  states. Within the GGA, the ground state is ferromagnetic, and is stabilized by Hund's coupling on the in-plane F atoms which occurs due to F participation in the magnetism resulting from the  $e_g - p_\sigma$  hybridization. The electronic structure is nearly half-metallic, and not insulating. It would be of interest to experimentally test the prediction of a metallic electronic structure.

The resulting picture of the electronic structure and magnetism is very different from the undoped cuprates. (1)  $\text{Cs}_2\text{AgF}_4$  has two active bands:  $d_{x^2-y^2}$  and  $d_{z^2}$ ; neither is exactly half-filled; (2) moment formation in  $\text{Cs}_2\text{AgF}_4$  is due to a Stoner type mechanism as opposed to on-site Coulomb repulsions that are crucial in the cuprates; (3) the magnetism has strong itinerant character due to F participation, as opposed to the local moment superexchange mediated character of cuprate antiferromagnetism; and (4) we find ferromagnetism with the ideal tetragonal structure; orbital ordering to obtain ferromagnetism within a superexchange mediated framework is not needed. We note that the predicted F contributions to the magnetism are large enough to be detected using neutron scattering.

Finally, we note that the mechanism for ferromagnetism in  $\text{Cs}_2\text{AgF}_4$  is quite robust, and would be expected to occur in other Ag(II) fluorides with similar bond lengths and topologies. Since it does not rely on small struc-

tural effects, it provides a ready explanation for the observed ferromagnetism in the other  $A_2\text{AgF}_4$  compounds. Furthermore, the above picture of itinerant magnetism may be more generally applicable to other Ag(II) fluoride compounds. For example,  $\text{KAgF}_3$  shows a metal insulator transition coincident with an antiferromagnetic ordering.<sup>4</sup> This is much more natural in an itinerant system than in a strongly correlated local moment system, which would tend to be insulating on both sides of the ordering temperature at odd integer band fillings. The structure of that compound shows compressed octahedra and Ag-F-Ag chains along the  $c$ -axis direction with short bond lengths. Assuming that the above mechanism applies also to this compound, one may expect ferromagnetic chains along  $c$ . Considering that the ground state is known to be antiferromagnetic, one may anticipate a C-type ordering of antiferromagnetic  $a-b$  planes, stacked ferromagnetically in that case. In any case, in perovskite derived Ag(II) fluorides, the mechanism that we propose would generally favor ferromagnetism or complex antiferromagnetic states, with ferromagnetic interactions along some bonding directions, as opposed to simple G-type ordering.

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